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【論文の内容の要旨】

Artificial Photosynthesis system sensitized by metal complexes is an area where a lot of active research is progressing and to realize such a sustainable solution for future energy crisis still requires ground breaking discoveries. One of the promising approaches to overcome the bottleneck issue regarding the photo oxidation of water, an important step in artificial photosynthesis, has been proposed to be a two electron oxidation of water driven by single photon. The success of 1hv/2e- photo-oxygenation of alkenes by Ru-Porphyrin complexes is inspirational in making efforts in this direction to develop a stable chemical architecture for artificial photosynthesis.

Water oxidation ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) is a potential half reaction in artificial photosynthesis but it imposes a significant mechanistic uphill in its requirement for both 4H+/4e- loss and O-O bond formation. Of the various approach to develop an efficient water-oxidation catalyst the electrochemical prospect is one of the finest strategy where the steady state electrolysis of water oxidation is investigated. One of the main challenges in the electrochemical oxidation of water is to develop an efficient system with lowest over-potential. It is also important that these water oxidation systems must be made of earth abundant material so it should be crucial to put effort in developing molecular catalyst using earth abundant elements like aluminum and silicon as metal

centers. Recently our group has succeeded in catalyzing electrochemical water oxidation using Aluminium porphyrins in basic conditions. Silicon as the second most earth abundant element and more electronegative will be more suitable and promising candidate to serve as a metal center for water activation. In my research I have synthesized and studied a series of silicon porphyrins, with anionic, cationic and neutral phenyl substituent a, to develop suitable molecule and conditions for water oxidation.

Although many reports regarding the synthesis and characterization of silicon porphyrins they were no studies on the catalytic ability of silicon porphyrins despite of their promising REDOX properties. The reason for the less studies on silicon porphyrins being the difficulty in synthesising silicon porphyrins. In my research the original multipot multistep synthesis was modified to a convenient single pot multistep synthesis. Also a reliable method to monitor the completion of each step by measuring the UV-Visible spectrum of reaction mixture was proposed. The synthesis of Lithium salt of freebase porphyrins, precursor of Si insertion, was modified from a high temperature reaction using solvents like Tetrahydrofuran and Dimethoxy ethane to a more convenient room temperature reaction using Dichloro methane (DCM). The formation siloxane bond was identified as a difficulty in synthesising silicon porphyrins in literature, a washing procedure using $NaOH/K_2CO_3$: DCM to break these siloxane bond was proposed.

Silicon porphyrin complexes with electron donating and electro withdrawing phenyl substituents with hydroxyl (–OH) as axial ligand have been developed for tuning the water oxidation potential. The axial ligand, –OH, can undergo protonation and deprotonation reaction upon decreasing and increasing pH condition respectively. The axial oxygen atom will act as the point of attack for acid (H^+) and base (OH^-) to undergo proton exchange equilibrium reactions. The axial ligand microenvironment of Silicon porphyrins in different pH condition was analyzed using absorption, emission and Proton Nuclear Magnetic Resonance spectroscopy. The studies show that the axial ligand undergoes pH dependent proton exchange reactions like aluminium porphyrins[4] and the pKa values for these protolytic equilibriums appear in acidic pH which is consistent with the more electronegative nature of silicon than aluminium (for aluminium pKa values appear in basic pH). The pKa values is dependent on the electron donating electron withdrawing nature of phenyl substituents and also on the extent of conjugation of phenyl substituent with porphyrin ring which depend upon the dihedral angle of phenyl substituent which in turn depend on the ortho substituents on phenyl

group . In addition to axial ligand the peripheral phenyl substituent will also undergo protonation in the case of SiTCPP (trans-dihydroxo [-tetracarboxyl phenyl porphyrinate] silicon (IV)) and SiTPyP(trans-dihydroxo [-tetra pyridyl porphyrinate] silicon (IV)). In case of SiTPyP a stepwise protonation of the pyridyl substituent was observed.

A detailed density functional theory (DFT) calculations (using Gaussian 09 B3LYP/6-31G* basis function) was carried out for each molecule and found that the one electron oxidised state of Silicon porphyrins will have the spin localized on the axial oxygen atom when one or both of the axial hydroxyl ligand is in completely deprotonated condition, this condition is more suitable for water activation

The electrochemical behavior under various solvent conditions was studied by cyclic voltammetry, in case of SiTPyP a very high catalytic behavior was observed at pH less than 3. The pH dependent oxidation potential change was studied, upon decreasing pH the oxidation peak shifted to more positive potential. The sudden changes in oxidation half reaction correspond to observed pKa values. The Pourbaix diagram for silicon porphyrins were constructed and proton coupled electron transfer reaction was identified. The Turn over frequency (TOF) of the molecule for the catalytic oxidation process was measured by modified Randless-Sevcik method. The TOF of the molecule shows an increasing trend with decreasing pH condition which is in agreement with the increasing oxidation potential. The TOF value suggests that efficient water oxidation can be observed under acidic conditions.